

Modeling Organic Chemical Fate in Aquatic Systems: Significance of Bioaccumulation and Relevant Time-Space Scales

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The importance of aquatic food chain bioaccumulation of organic chemicals in contributing to human dose is derived. It is shown that for chemicals with log octanol water partition coefficients greater than about 3, the role of food chain transfer to fish consumed by humans becomes the more dominant route over drinking water. Modeling of aquatic food chain bioaccumulation then becomes necessary to accurately estimate dose of such chemicals to humans. The relevant time and space scales for groundwater and surface water also indicate a division of organic chemicals at a log octanol water partition coefficient of about 3. For chemicals greater than that level, groundwater transport is minimal, while for chemicals with log octanol water coefficients of less than about 3, detention times are long relative to surface water and biodegradation processes become more significant. An illustration is given of modeling the groundwater transport of two organic chemicals (BCEE and benzene) and a metal (chromium) at a Superfund site. The model indicates that after 10 years only a relatively small fraction of the chemicals had traveled in the groundwater about 300 m to the point of release from the site to surface water. On the other hand, steady state in the adjacent stream and lake is reached rapidly over a distance of 2000 m, illustrating the difference in spatial and temporal scales for the groundwater and surface water. — *Environ Health Perspect* 103(Suppl 5):53–57 (1995)

Key words: model, bioaccumulation, chemical fate, time-space scales, dose, risk assessment

Introduction

The basic problem in the management and control of organic chemicals in aquatic systems is the prediction of the effectiveness of proposed remedial actions. The effectiveness of such actions is, of necessity, measured against a specific target water quality concentration or a target acceptable level of chemical intake by humans. Credible predictions of remedial action effectiveness must be based on credible understanding of processes that contribute

to chemical fate, transport, and accumulation. Mathematical models of the key features of chemical behavior in aquatic systems can often be of significant value in providing quantitative predictions of proposed environmental controls. Mathematical models can also be used to delineate the boundaries of chemical problem contexts to aid decision making and research efforts. For example, the relative importance of organic chemical dose to humans from drinking water or from consumption of contaminated aquatic foodstuffs can be described with a modeling framework. Also, the substantive differences between chemical fates in groundwater and surface water systems can be evaluated together with the temporal and spatial conditions under which specific processes are relevant.

This paper addresses these latter two issues: the range of organic chemicals for which aquatic food web bioaccumulation is significant, relative to drinking water, in evaluating the allowable dose for protection of human health; and the relevant time and space scales of organic chemical fate in groundwater and surface water and the significance of processes such as chemical partitioning and biodegradation at such scales in the respective water systems. The issues are evaluated through use of a general modeling framework of fate and accu-

mulation of toxic chemicals in the aquatic environment.

The Relative Importance of Bioaccumulation of Organic Chemicals in Dose to Humans

It has become increasingly clear over the past several decades that certain organic chemicals may accumulate in aquatic food webs to levels significantly above those expected from equilibrium exposure to water only (1–3). Such accumulation has been attributed to transfer in the aquatic food chain and has been verified by modeling such transfers in specific systems, such as lake trout in the Great Lakes (4), striped bass in the Hudson (5), and the food web of New Bedford Harbor (6). A relevant question then is: To what degree is the process of bioaccumulation of organic chemicals significant in the allowable dose to humans? The application of a simple model of bioaccumulation in a four-level food chain provides a means for addressing this question.

A dose R (i.e., a dose for noncarcinogenic chemicals as a reference dose) or a dose for a given increased cancer risk, R'/q^* [for q^* as the carcinogenic potency (mg/kg-day^{-1})] that results from ingestion of chemicals in water and aquatic-related

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food (e.g., fish) by humans is written as

$$R = (I_{wt}c + I_f v) / W \quad [1]$$

for I_{wt} as water ingestion rate (l/day), c as the water chemical concentration (mg/l), I_f as the food ingestion rate (kg/day), v as the chemical concentration in the fish (mg/kg), and W as the human weight (kg). The chemical concentration in the food can be related to the water chemical concentration by the bioaccumulation factor (BAF) as

$$N = v/c \quad [2]$$

where N (mg/kg ÷ mg/l = l/kg) represents the accumulation in the fish due to aquatic food web interactions relative to the water concentration. For nonionic organic chemicals, the lipid-normalized BAF, N_l , recognizes the tendency for such chemicals to partition primarily into the lipid pools of organisms and is given by

$$N_l = N/f_l \quad [3]$$

for f_l as the fraction of lipid (wet weight) in the fish.

Thus, Equation 1 can be written as

$$R = [(I_{wt} + I_f N_l f_l) / W] c \quad [4]$$

Now the lipid normalized BAF can be related to the octanol water partition coefficient of the chemical K_{ow} through a model of the chemical transfer and accumulation in the aquatic food web (3,7). Such work indicates that N_l is given approximately as follows:

$$\begin{aligned} N_l &\approx K_{ow} \text{ for } \log K_{ow} < 3-4 \\ &= g(K_{ow}) \text{ for } \log K_{ow} > 3-4 \end{aligned} \quad [5]$$

where $g(K_{ow})$ is the food web biomagnification function. The biomagnification represents the increase in the BAF due to food web transfer of the chemical and is a function of aquatic trophic level and interactions. For a simple four-level food chain, with organic chemicals that are not metabolized by aquatic organisms, the lipid normalized BAF for the top predator may increase to levels of 10 times or more above K_{ow} , with the range in $\log K_{ow}$ from about 4 to 6.5. Beyond $\log K_{ow}$ of about 6.5, the biomagnification function decreases due to reduced dietary chemical assimilation efficiency by the fish. The chemical dose to humans relative to the water concentration

(Equation 4) is therefore a function of the octanol water partition coefficient as given by

$$R/c = [I_{wt} + I_f f_l g(K_{ow})] / W \quad [6]$$

For application of this equation, it is assumed that the chemicals are not metabolized by aquatic organisms. From Equation 5, N_l is set equal to K_{ow} over the range of $\log K_{ow}$ from -1 to 4. Beyond this K_{ow} level, N_l is set equal to a smoothed function of observed data and guided by the bioaccumulation model of a four-level food chain. Figure 1 shows a water only normalized plot of this function for the following additional conditions: $I_{wt} = 2$ l/day, $I_f = 6.5$ g fish/day, $f_l = 0.05$, and $W = 70$ kg. As seen, the relative importance of the water and food route to the water route increases substantially for chemicals with $\log K_{ow}$ greater than about 3. For chemicals less than this level, ingestion of contaminated water is most significant. For $\log K_{ow}$ greater than about 3, the consumption of contaminated fish rather than ingestion of drinking water becomes the dominant source of chemical. Since remedial actions involve reductions in water concentration to meet target acceptable doses (Equation 4), it is concluded that such proposed reductions will have to recognize the potential significant accumulation of higher K_{ow} chemicals.

Illustration: Bioaccumulation of PCBs in Striped Bass in the Hudson Estuary

A modeling analysis and prediction of the PCBs ($\log K_{ow}$:4.5–7.1) in the striped bass of the Hudson estuary (5) illustrates the accumulation of a chemical in a top predator that is consumed by humans. The model consists of homologue-specific PCB fate and transport calculations for the Hudson water column and sediment, including PCB volatilization. Other loss mechanisms such as biodegradation were evaluated and found not to be significant. Subsequent transfer and bioaccumulation of PCB homologue is calculated by a time- and age-dependent model of the migratory striped bass food web. The principal conclusions from that work were that more than 90% of the observed concentrations in the striped bass were due to bioaccumulation. Predictions were made of how long it would take for the striped bass PCB concentration to reach acceptable levels. Those predictions indicated that a “no action” alternative would result in acceptable PCB levels being reached by the mid-1990s.

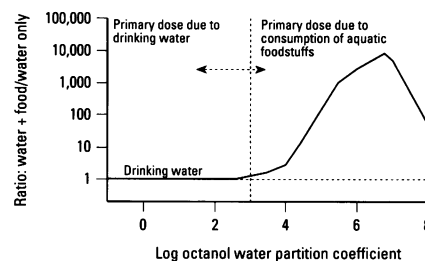


Figure 1. Relationship between ratio of chemical dose/water concentration and the octanol water partition coefficient. See Equation 6 and text for parameter values.

Figure 2 summarizes the results and includes more recent subsequent data that is used to check the trend of the original prediction. As indicated, virtually all of the concentration is calculated to be from food web bioaccumulation, and a relatively negligible amount is due to exposure to water only. The subsequent data collected in 1988 and 1990 indicate a general confirmation of the prediction, at least up to that time. Continual verification of predictions of this type of model will lend additional support to the preceding analysis on the significance of bioaccumulation in chemical dose to humans.

Relevant Time-Space Scales for Fate, Transport, and Accumulation of Organic Chemicals

Since the $\log K_{ow}$ of about 3 is a significant dividing point for the relative importance of drinking water and aquatic food ingestion for nonmetabolizable organic chemicals, it is of interest to examine the behavior of these two broad groups of chemicals regarding their fate, transport, and accumulation in aquatic systems.

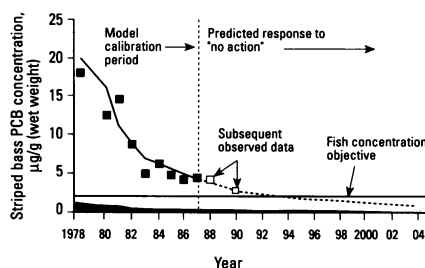


Figure 2. Model calibration and comparison of prediction to data collected subsequent to model analysis for total PCB in Hudson estuary striped bass. Hatched area is contribution to total concentration due to exposure to water only.

The basic model for the physiochemical fate and transport of chemicals in aquatic systems incorporates partitioning between freely dissolved chemicals and chemicals in the particulate form, advective and dispersive transport, loss processes (e.g., volatilization), and decay and transformation processes (e.g., biodegradation, photolysis). There are fundamental differences between the transport and fate of chemicals in groundwater and surface water systems. Principally, for groundwater, the solids on which the chemical is sorbed are stationary (although there may be transport of small amounts of particulates in some instances); for surface water the solids are moving with the advective velocity. Also, for surface water, there may be significant interactions with aquatic sediments.

Chemical Partitioning

For both systems, a simple partitioning between dissolved and particulate chemical forms is given by considering the total chemical (c_T , mg/l) as the sum of dissolved (c_d , mg/l) and particulate (c_p , mg/g), i.e.,

$$c_T = rm + \phi c_d' \quad [7]$$

where m is the solids concentration (mg/l) or bulk density and ϕ is the porosity. For linear partitioning, the fraction of chemical in dissolved form (f_d) and in particulate form (f_p) is then

$$f_d = (1 + (\pi/\phi)m)^{-1} \quad [8a]$$

$$f_p = 1 - f_d \quad [8b]$$

where π is the partition coefficient (l/kg[dry weight]). It can be assumed that the most significant phase for partitioning of organic chemicals is the organic carbon phase and that the carbon-normalized partition coefficient is approximately equal to the octanol water partition coefficient for fractions of organic carbon greater than about 0.5%. Therefore,

$$\pi_{oc} \approx K_{ow} \quad [9a]$$

$$\text{and} \quad \pi_{oc} = \pi/f_{oc} \quad [9b]$$

where f_{oc} is the fraction of organic carbon in the solids. The fraction dissolved is then

$$f_d = [1 + (f_{oc}K_{ow}/\phi)m]^{-1} \quad [10]$$

Groundwater systems have high concentrations of fixed solids and low concentrations of organic carbon relative to surface

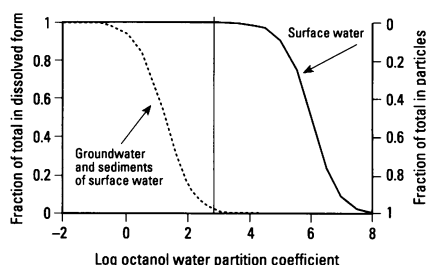


Figure 3. Relationship between fraction of organic chemical in dissolved and particulate forms and log K_{ow} . See Equation 10 and text for parameter values.

water, with relatively low concentrations of moving solids. Assume that groundwater contains solids of 1,750,000 mg/l (i.e., bulk density of 1.75 kg/l, for solids with a density of 2.5 g/cm³ and a porosity of 0.3) and has an f_{oc} of 0.01 and that surface water has solids concentrations of 10 mg/l, a porosity of 1.0, and an f_{oc} of 0.1; the relationship given by Equation 10 is shown in Figure 3.

As shown for groundwater with chemicals of log K_{ow} greater than about 3, all of the chemical is partitioned onto the particles, with little chemical in the dissolved phase. For surface water, such a condition does not prevail until log K_{ow} of about 8. Also, for chemicals in surface water with log K_{ow} of less than about 3, almost all of the chemical is in the dissolved phase.

Physiochemical Fate Equations

The significance of this partitioning behavior in surface water and groundwater can be seen by examining the fundamental equations used in modeling the fate and transport of chemicals in aquatic systems. For simplicity, a one-dimensional representation is given. For surface water and groundwater, respectively, the equations are

$$\frac{\partial c_{Ts}}{\partial t} = E_s \frac{\partial^2 c_{Ts}}{\partial x^2} - U_s \frac{\partial c_{Ts}}{\partial x} - K_s c_{Ts} \quad [11a]$$

$$\frac{\partial c_{Tg}}{\partial t} = f_{dg} E_g \frac{\partial^2 c_{Tg}}{\partial x^2} - f_{dg} U_g \frac{\partial c_{Tg}}{\partial x} - K_g c_{Tg} \quad [11b]$$

with c_T as the total chemical concentrations in surface water and groundwater indicated by the subscripts s and g , respectively; E is the dispersion coefficient of the chemical; U is the advective velocity; K represents all kinetic mechanisms (e.g., biodegradation)

Table 1. Order of transport parameters for different aquatic systems.

	Ground-water	Surface water	Aquatic sediments
Advective velocity	m/day	km/day	cm/year
Dispersion	m ² /day	km ² /day	cm ² /day
Residence time	Years—decades	Days—years	Months—years
Solids for sorption, mg/l	1,000,000 (Stationary)	1–100 (Moving)	250,000 (Eroding-depositing)

as a first-order process; and f_{dg} is the fraction of total chemical that is dissolved in the groundwater. The basic difference between the two aquatic systems is made clear by these equations. For surface water, the solids are moving with the velocity, so the total chemical is dispersed and advected. In contrast, the solids in groundwater systems are generally stationary, and only the dissolved component is transported. Table 1 shows the relative parameters associated with these two systems plus the aquatic sediments underlying surface waters. Such sediments behave similarly to the groundwater systems. Combining the values in this table with Figure 3 and Equation 11, it can readily be concluded that chemicals with log K_{ow} greater than about 3 will not be transported any significant distances in groundwater. (That is, for log K_{ow} greater than 3, f_{dg} approaches 0 (Figure 3); Equation 11b shows that the dispersion and advection of such chemicals in groundwater is minimal.) Such chemicals in groundwater will therefore tend to remain where placed. On the other hand, for surface water, all chemicals are transported with the prevailing dispersion and advective mechanisms.

The net result is summarized in Figure 4, which shows the approximate time to travel a given distance from a discharge

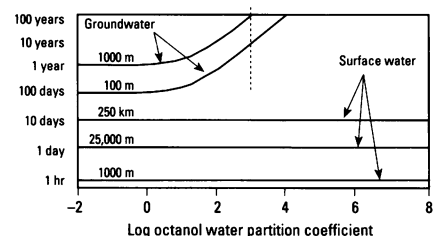


Figure 4. Approximate time for an organic chemical to travel a given distance in groundwater and surface water as a function of log K_{ow} . Parameters similar to those for Figure 3 with $U_g = 1$ m/day and $U_s = 25$ km/day.

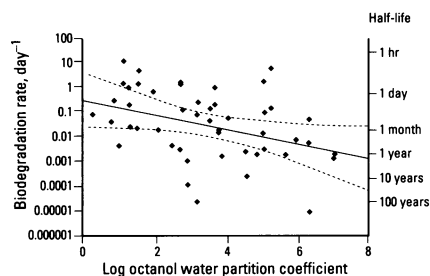


Figure 5. Variation of biodegradation rates for some organic chemicals as a function of octanol water partition coefficient.

location for groundwater and surface water. Again, a clear dividing region exists where chemicals with $\log K_{ow}$ greater than about 3 do not move beyond about 1000 m over a period of 100 years.

Figure 5 shows some data on biodegradation rates as a function of $\log K_{ow}$. The data drawn from several sources (8–12) are not exhaustive and are only illustrative. Both surface water and groundwater are included, and the largest fraction of the data is from the pesticide chemical group. The variation and scatter are large and the relationship is statistically poor ($r^2 = 0.14$, $p = 0.008$), but it does tend to indicate a general downward trend with increasing K_{ow} . Comparing Figures 4 and 5, it can be seen that for surface water biodegradation half-lives of greater than about a month will not significantly degrade in the normal time it takes for water to move through surface water. Conversely, for groundwater, with the long detention times over short distances, the effectiveness of a process such as biodegradation is greatly enhanced.

Illustration: Groundwater–Surface Water Superfund Site

Chemicals were dumped at a site in southern New Jersey (the Lipari Superfund site), which subsequently contaminated an aquifer, local streams, and a nearby lake and also volatilized organic chemicals (e.g., benzene) from a marsh, which was fed by the groundwater and interacted with a surface stream (13,14). Preliminary modeling was conducted to determine principal routes of transport and loadings to the stream and the atmosphere (15). Figure 6 shows a computed flow field for a 928-segment representation of the site (aquifer average velocity about 0.3 m/day), which interacts with two small streams. The principal stream is Chestnut Branch, which has a flow of about 0.2 m³/sec and subse-

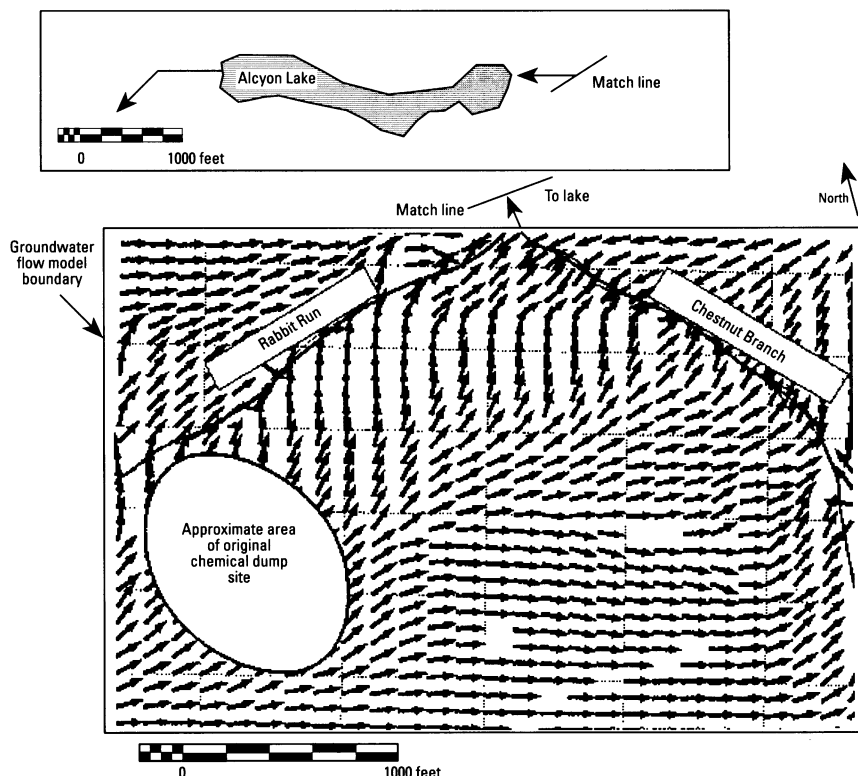


Figure 6. Computed groundwater flow field for a 928-segment model of a Superfund site.

quently discharges into Alcyon Lake, about 300 m downstream. The flow field shown in Figure 6 predates the installation of a slurry wall to reduce the emission of chemical from the area. Figure 7 shows an illustrative calculation for three chemicals: bis(2-chloroethyl)ether (BCEE), benzene, and chromium. For BCEE and benzene, respectively, $\log K_{ow}$ values are 1.6 and 2.1 and partition coefficients are 0.2 and 0.7 for fraction organic carbon of 0.005. The results shown in Figure 7 are for conservative behavior of all three chemicals and represent the calculated time variable

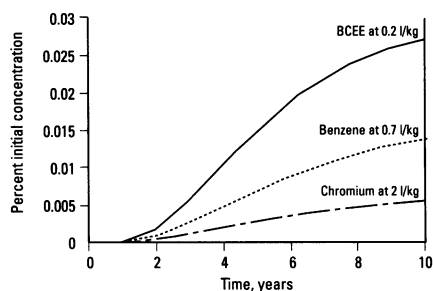


Figure 7. Calculated concentrations of three chemicals at a location adjacent to Chestnut Branch using the flow field of Figure 6 and indicated partition coefficients.

behavior for a segment (about 300 m from the dump site) in the marsh region adjacent to Chestnut Branch. As indicated, after 10 years of release at the dump site, the concentrations are still far below equilibrium values, and the retardation of the chemicals as a function of partitioning is evident. It is also clear that chemicals with $\log K_{ow}$ of 3 or greater would not move any significant distance at all in this setting.

Thus, after 10 years, a relatively small fraction (but still of concern) of the chemicals had traveled only about 300 m to the point of release from the site to the surface water. Once the breakthrough occurred to the marsh area, and subsequently to Chestnut Branch (and to the atmosphere), time of travel increases greatly (at stream velocity of about 7500 m/day and at lake velocity of about 150 m/day), and concentrations in the stream and lake rapidly reach steady state. Figure 8 shows a steady-state model calculation for BCEE in Chestnut Branch and Alcyon Lake using an estimated 5.5 kg/day distributed along the discharge interaction with the stream. The comparison of the calculated BCEE concentration at steady state to the observed data for this period is good and

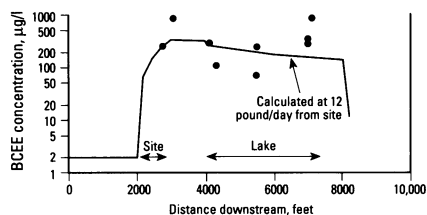


Figure 8. Comparison of calculated BCEE concentration at steady state with observed data in stream and lake. See Figure 6 for location map.

confirms the rapid passage to steady state over an approximately 2000-m distance.

Conclusions

The significance of hydrophobic organic chemical dose to humans can be related to the octanol water partition coefficient. This characteristic of chemicals is representative of the tendency for such chemicals to partition into organic carbon and lipid pools. Modeling the accumulation of such chemicals in aquatic systems indicates that for chemicals with $\log K_{ow}$ greater than about 3, the dose to humans is almost entirely controlled by consumption of contaminated fish. Modeling of the accumulation of such chemicals is therefore necessary to predict the effectiveness of remediation programs on reducing chemical concentrations in the top predators of aquatic food webs. The dividing point of $\log K_{ow}$ greater

than about 3 is also significant in dividing organic chemical fate and transport between groundwater and surface water. Thus, for chemicals with $\log K_{ow}$ greater than about 3, groundwater transport is minimal because of the high partitioning to groundwater sorption sites. Similarly, detention times in groundwater for chemicals with $\log K_{ow}$ less than about 3 are long and potentially suitable for bioremediation. Surface water, on the other hand, has a relatively short detention time and all chemicals move rapidly through such systems. As a result, the effect of biodegradation processes on the fate of organic chemicals in surface water is therefore small, although such processes may be important in aquatic sediments.

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